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# Food Chemistry

Analytical Methods

# Analytical strategies for determination of cadmium in Brazilian vinegar samples using ET AAS

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A B S T R A C T

This paper proposes two methods for determination of cadmium in vinegar employing electrothermal atomic absorption spectrometry. The optimization step was performed using two-level full factorial and Box–Behnken designs, being that a new multiple response function was established. Under experimental conditions of pyrolysis temperature of 640 °C and atomization temperature of 2000 °C, the direct method allows the analysis using the external calibration technique, with limit of quantification of 14 ng L$^{-1}$ and characteristic mass of 1.2 pg, having aluminium as chemical modifier. This method was applied in six samples of vinegar acquired from Salvador City, Brazil. The cadmium content varied from 20 to 890 ng L$^{-1}$. Other method was also proposed by digestion using nitric acid and hydrogen peroxide in reflux system employing cold finger, being cadmium determined by ETAAS. The results obtained with the complete digestion procedure were in agreement with those found by the direct method proposed herein.

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## 1. Introduction

Vinegar is a condiment used in food preparation throughout the world. Generally, vinegar is produced by the fermentation of raw plant materials such as grapes, apples and sugarcane, among others. Vinegar is primarily composed of acetic acid and ethyl alcohol. The mineral content is derived from the plant material used and from contamination during the production process and storage. Given the importance of vinegar in human food, several methods for the determination of the levels of toxic chemical elements in this condiment have been proposed. A paper evaluated different sample preparation procedures for the determination of lead concentrations in vinegar using ICP-MS and GFAAS (Ndung'u, Hibdon, & Flegal, 2004). Another study determined and evaluated possible sources of lead in vinegar (Ndung'u, Hibdon, & Flegal, 2007). A method using stripping chronopotentiometry was proposed for determination of lead, cadmium, copper and zinc in commercial Iranian vinegars (Saei-Dehkordi, Fallah, & Ghafari, 2012). A direct method for the determination of lead in vinegar by ETAAS was established employing bismuth as internal standard, and the chemical modification was performed with ruthenium as the

permanent modifier and co-injection of palladium–magnesium (de Oliveira & Gomes Neto, 2007). Another work of the same research group used tungsten as permanent chemical modifier and co-injection of palladium–magnesium also for direct determination of lead in vinegar (Oliveira, Oliveira, & Gomes Neto, 2007). In a method proposed for the determination of cadmium and lead in vinegar leached from pewter cups by ET AAS the chemical modification was performed using palladium–magnesium (Dessuy et al., 2011).

The Box–Behnken design is a chemometric tool often used for the optimization of analytical methods (Garcia-Rodrigues, Cela-Torrijos, Lorenzo-Ferreira, & Carro-Diaz, 2012; Khajeh, 2011; Kishore & Kayastha, 2012; Singh et al., 2014; Zarena, Sachindra, & Udaya Sankar, 2012). This tool enables quadratic models showing the critical condition (maximum, minimum or saddle point) to be obtained (Ferreira et al., 2007). The optimization of analytical methods involving two or more chemometric responses requires use of multiple responses. These multiple responses are established by considering the objective of the analytical system that is being optimized. The most common method employed to obtain multiple responses makes use of a desirability function $D$, where individual response surfaces are determined for each response (Derringer & Suich, 1980). An on-line sequential preconcentration system using chemically modified silica was developed for determination of Cr(III) and Cr(VI) by flame atomic absorption

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spectrometry. The optimization was performed using a multivariate methodology and a desirability function was established (Tarley et al., 2012).

In this study, two methods for determination of cadmium in vinegar using ETAAS were proposed. Also a new strategy was established to qualitatively and quantitatively evaluate the peak profiles obtained during the optimization step.

## 2. Experimental

### 2.1. Instrumental parameters of the ET AAS

The experiments were performed using a ZEEnit 600 atomic absorption spectrometer (Analytik Jena AG, Jena, Germany) equipped with a graphite atomizer with transverse heating and Zeeman effect background correction. A MPE 60 automatic liquid autosampler (Analytik Jena AG, Jena, Germany) was used to introduce the samples. In all analyzes, pyrolytic graphite-coated tubes and a L'vov platform were employed. A cadmium hollow cathode lamp (Varian, Mulgrave, VA, Australia) with wavelength of 228.8 nm and a spectral bandwidth of 0.5 nm was used as the radiation source. Argon (purity, 99.997%) at an internal flow rate of $2.0 \, L \, min^{-1}$ was used as the purge gas during all steps (White Martins, Salvador, Brazil) except atomization, during which the flow was stopped. The protocol proposed in this work is presented in Table 1.

### 2.2. Reagents and solutions

All solutions and standards used were prepared with high-purity water obtained from a Milli-Q system (Millipore, Bedford, USA) and had a specific resistivity of 18 MΩ-cm. All reagents used were of the highest analytical grade. The standards were prepared by the successive dilution of a $1000 \, mg \, L^{-1}$ stock solution of cadmium (Merck, Darmstadt, Germany) in in 0.5% nitric acid. A volume of three microlitres of a $1000 \, mg \, L^{-1}$ ICP-MS aluminium solution (Merck) was used as chemical modifier (da Silva et al., 2011; Ferreira et al., 2011; Lima et al., 2013), being that the samples and standards volumes injected in the graphite furnace for the direct method was 20.0 μL. The accuracy of method was evaluated using a certified reference material of bovine liver furnished by the National Institute of Standard and Technology.

### 2.3. Sample digestion using digester block and reflux system

Samples were digested using a digester block and a reflux system that included a cold finger (Ferreira et al., 2013). Aliquots (5 mL) of each sample were placed into individual glass tubes. 4 mL of concentrated nitric acid (Merck) and 2.0 mL of 30% (v/v) hydrogen peroxide (Merck) were added to each tube. The samples were then digested for 60 min at 110 °C. Subsequently, the digested samples were transferred to a 25-mL volumetric flask, and ultrapure water was then used to fill the volumetric flask to

25 mL. During the determination of cadmium the sample volume injected in the graphite furnace was also 20.0 μL.

### 2.4. Determination of the qualitative evaluation index (QEI)

Given that the "ideal peak" for ET AAS methods should be large (a greater integrated area ensures greater sensitivity) and narrow (resulting from a process of fast atomization), the qualitative evaluation index was calculated as the ratio of the height of the peak to the width of the peak at half maximum. Fig. 1 shows the expression for calculating the QEI.

$$QEI = (\textbf{\textit{a}}/2)/\textbf{\textit{l}} \tag{1}$$

where $\textbf{\textit{a}}$ is the height of the peak and $\textbf{\textit{l}}$ is the width of the peak at half maximum.
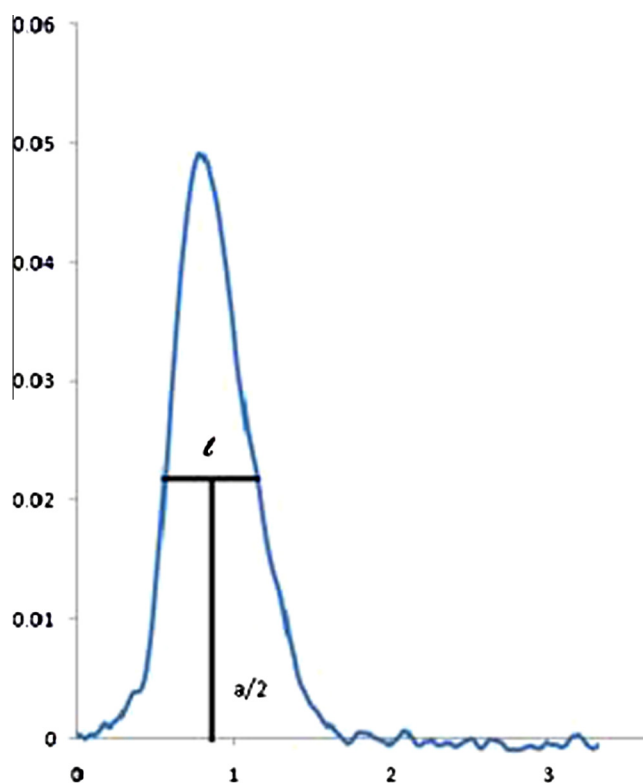
The height and width of each peak were measured using EXCEL to five significant digits.

The multiple response (MR) was calculated by normalising the integrated absorbance and the QEI to the highest values of these parameters found in the experiments.

$$MR = (abs/abs_{maximum}) + (QEI/QEI_{maximum}) \tag{2}$$

### 2.5. Optimization of the experimental conditions

The optimization of the experimental conditions established for the determination of cadmium employing ETAAS were performed using two-level full factorial design for preliminary evaluation of the factors and also Box–Behnken design for determination of the critical conditions of these factors. All experiments were performed in random order. Chemometric data were processed using the statistical program Statistica 6.0.

**Table 1**
Temperature program used for cadmium content determinations; an internal gas flow rate of $2.0 \, L \, min^{-1}$ was used in all stages except during atomization, when the gas flow was turned off.

| Step | Temperature (°C) | Ramp (°C/s) | Hold time (s) |
|------|------------------|-------------|---------------|
| Drying | 110 | 15 | 10 |
| Drying | 120 | 10 | 15 |
| Pyrolysis | 640 | 100 | 7 |
| Atomization | 2000 | FP[a] | 4 |
| Cleanout | 2550 | FP | 5 |

[a] Full power.



**Fig. 1.** Determination of QEI in analytical signal obtained for cadmium by ETAAS.

## 3. Results and discussion

### 3.1. Optimization of the instrumental conditions for the determination of cadmium concentrations

The instrumental factors involved in the determination of the cadmium concentration in vinegar by ET AAS were optimized in two steps. First, a two-level full factorial design was performed with the following variables: aluminium modifier mass, pyrolysis time, pyrolysis temperature and atomization temperature. In the step second, a Box–Behnken design was also used to determine the critical conditions for these factors.

The two-level full factorial design ($2^4$) was established, with four additional experiments at the central point. The experimental variables as coded and real values for the four factors and several chemometric responses are shown in Table 2.

The effects of the factors and their p values when employing the absorbance as the chemometric response were calculated and the results are shown in Table 3.

These data demonstrate that all these factors have statistically significant effects on the analytical signal under the experimental conditions established. The atomization temperature had a positive effect, which was the largest among the four factors. The positive effect indicates that an increase in the atomization temperature contributes to an increase in the absorbance. This relationship can be observed by comparing the absorbances obtained at temperatures of 1300 and 1800 °C. The other factors were significant; however, the magnitudes of these effects were considerably smaller than that of the effect of the atomization temperature.

An evaluation of the factorial design was also performed using only the QEI as the chemometric response. The effects for the four factors and their p values are also summarized in Table 3.

The effect values obtained demonstrate that all four factors were statistically significant. The atomization temperature had a positive effect, and it had the greatest influence on the peak shape. The data presented in Table 2 show that the highest QEIs were obtained at an atomization temperature of 1800 °C. The modifier mass was the second most important factor that affects the value of the QEI. This factor had a negative effect, and thus,

**Table 3**
Effect values for the principal factors using the three chemometric responses.

| | Effects* | P |
|---|---|---|
| *Integrated absorbance* | | |
| Atomization temperature | 0.03442 ± 0.00082 | 0.000001 |
| Modifier mass | −0.00321 ± 0.00082 | 0.001099 |
| Pyrolysis time | −0.00300 ± 0.00082 | 0.001336 |
| Pyrolysis temperature | 0.00130 ± 0.00082 | 0.014910 |
| | | |
| *Qualitative evaluation index (QEI)* | | |
| Atomization temperature | 0.03739 ± 0.00027 | 0.000000 |
| Modifier mass | −0.01404 ± 0.00027 | 0.000000 |
| Pyrolysis time | −0.00506 ± 0.00027 | 0.000011 |
| Pyrolysis temperature | 0.00476 ± 0.00027 | 0.000013 |
| | | |
| *Response multiple* | | |
| Atomization temperature | 1.31916 ± 0.01747 | 0.00000 |
| Modifier mass | −0.28678 ± 0.01747 | 0.000015 |
| Pyrolysis time | −0.14301 ± 0.01747 | 0.000124 |
| Pyrolysis temperature | 0.10183 ± 0.01747 | 0.000342 |

* Expressed as interval confidence at 95% level.

the highest values for the QEI were obtained using 3 ng as the modifier mass.

The factorial design was also evaluated using the multiple response function (MR) as the chemometric response. The effects for the four factors considering this response are also showed in Table 3.

These results obtained for the effects using the multiple response function (MR) are compatible with those found using the integrated absorbance and the QEI as the chemometric responses. The atomization temperature and the modifier mass are the principal factors affecting the atomization of cadmium.

Considering all the results obtained using the factorial design, a Box–Behnken design was used to determine the critical conditions in the determination of the cadmium concentration in vinegar employing ET AAS. The experimental values established for the factors and the data obtained during the experiments are shown in Table 4.

The data obtained from the Box–Behnken design were evaluated using the multiple response as the chemometric response. This design generated the quadratic model

**Table 2**
Full two-level factorial design – optimization of the experimental conditions for cadmium determination.

| Exp. | Py-t | At-t | Modifier mass | Py-time | Abs. | QEI | Abs-n | QEI-n | Multiple response |
|---|---|---|---|---|---|---|---|---|---|
| 1 | −1 (400) | −1 (1300) | −1 (3) | −1 (5) | 0.00975 | 0.00210 | 0.2092 | 0.0322 | 0.2414 |
| 2 | −1 (400) | −1 (1300) | −1 (3) | 1 (15) | 0.00505 | 0.00400 | 0.1084 | 0.0621 | 0.1705 |
| 3 | −1 (400) | −1 (1300) | 1 (7) | −1 (5) | 0.00298 | 0.00690 | 0.0639 | 0.1071 | 0.1710 |
| 4 | −1 (400) | −1 (1300) | 1 (7) | 1 (15) | 0.00117 | 0.00130 | 0.0251 | 0.0202 | 0.0453 |
| 5 | −1 (400) | 1 (1800) | −1 (3) | −1 (5) | 0.04660 | 0.06090 | 1.0000 | 0.9457 | 1.9456 |
| 6 | −1 (400) | 1 (1800) | −1 (3) | 1 (15) | 0.04195 | 0.04970 | 0.9002 | 0.7717 | 1.6720 |
| 7 | −1 (400) | 1 (1800) | 1 (7) | −1 (5) | 0.04275 | 0.03210 | 0.9174 | 0.4984 | 1.4158 |
| 8 | −1 (400) | 1 (1800) | 1 (7) | 1 (15) | 0.04124 | 0.02360 | 0.8850 | 0.3665 | 1.2514 |
| 9 | 1 (800) | −1 (1300) | −1 (3) | −1 (5) | 0.01316 | 0.01730 | 0.2824 | 0.2686 | 0.5510 |
| 10 | 1 (800) | −1 (1300) | −1 (3) | 1 (15) | 0.01337 | 0.01150 | 0.2869 | 0.1786 | 0.4655 |
| 11 | 1 (800) | −1 (1300) | 1 (7) | −1 (5) | 0.00690 | 0.00400 | 0.1481 | 0.0621 | 0.2102 |
| 12 | 1 (800) | −1 (1300) | 1 (7) | 1 (15) | 0.00663 | 0.00300 | 0.1423 | 0.0466 | 0.1889 |
| 13 | 1 (800) | 1 (1800) | −1 (3) | −1 (5) | 0.04288 | 0.06440 | 0.9202 | 1.0000 | 1.9202 |
| 14 | 1 (800) | 1 (1800) | −1 (3) | 1 (15) | 0.03675 | 0.04590 | 0.7886 | 0.7127 | 1.5014 |
| 15 | 1 (800) | 1 (1800) | 1 (7) | −1 (5) | 0.04367 | 0.03220 | 0.9371 | 0.5000 | 1.4371 |
| 16 | 1 (800) | 1 (1800) | 1 (7) | 1 (15) | 0.03850 | 0.04040 | 0.8262 | 0.6273 | 1.4535 |
| 17 | 0 (600) | 0 (1550) | 0 (5) | 0 (10) | 0.02831 | 0.00780 | 0.6075 | 0.1211 | 0.7286 |
| 18 | 0 (600) | 0 (1550) | 0 (5) | 0 (10) | 0.02812 | 0.00740 | 0.6034 | 0.1149 | 0.7183 |
| 19 | 0 (600) | 0 (1550) | 0 (5) | 0 (10) | 0.02929 | 0.00750 | 0.6285 | 0.1165 | 0.7450 |
| 20 | 0 (600) | 0 (1550) | 0 (5) | 0 (10) | 0.02857 | 0.00760 | 0.6131 | 0.1180 | 0.7311 |

Py-t: pyrolysis temperature; At-t: atomization temperature; Py-time: pyrolysis time; Abs: integrated absorbance; QEI: qualitative evaluation index; Abs-n; normalisation of the integrated absorbance; QEI-n: normalisation of the qualitative evaluation index.

$$MR = -17.975 + 0.010(T_{pyro}) - 8.10.10^{-6}(T_{pyro})^2 + 0.016(T_{atom})$$
$$- 4.09.10^{-6}(T_{atom})^2$$

which has a maximum multiple response for the following experimental conditions: atomization temperature: 1980 °C, modifier mass: 2.89 μg, pyrolysis temperature: 641 °C and pyrolysis time: 7.01 s. This model was calculated using real values and only significant terms are being expressed. It has no lack of fit.

Based on these results, the experimental conditions chosen for the ET AAS method were as follows: atomization temperature: 2000 °C, modifier mass: 3 μg, pyrolysis temperature: 640 °C and pyrolysis time: 7 s.

### 3.2. Validation studies

Using the experimental conditions identified in the optimization step, the method allowed the determination of cadmium in vinegar with a characteristic mass of 1.2 pg, being, the limits of detection (LOD) and quantification (LOQ) of 4 and 14 ng L$^{-1}$, respectively, for a sample volume of 20.0 μL. These limits were determined as being LOD = $(3\sigma/s)$ and LOQ = $(10\sigma/s)$, where $(\sigma)$ is the standard deviation for the measurements from the blank solutions and $(s)$ is the slope of the external calibration curve. The precision (expressed as relative standard deviation) varied from 1.07% to 2.33% as can be seen in Table 5.

The matrix effect was evaluated using the analyte addition technique to choose the calibration technique for this method. Cadmium solutions with final concentrations in the range of 0–500 ng L$^{-1}$ were added to vinegar samples, and the cadmium concentration of each sample was determined with the direct method proposed herein. In this experiment, the equation of the analytical curve (expressed at the 95% confidence level) was as follows:

$$Abs = (0.0743 \pm 0.0035).C + (0.0048 \pm 0.0011), R^2$$
$$= (0.9989 \pm 0.0005),$$

where Abs is integrated absorbance and $C$ is the cadmium concentration in μg L$^{-1}$. An external calibration curve was determined using aqueous standards in the same concentration range, and the equation obtained was as follows:

$$Abs = (0.0726 \pm 0.0039).C + (0.0012 \pm 0.0010), R^2$$
$$= (0.9989 \pm 0.0005).$$

These experiments demonstrated that the external calibration technique can be used for the determination of cadmium concentrations in vinegar samples, as the analytical curve was linear up to 1500 ng L$^{-1}$.

The method accuracy for analyse of vinegar was not confirmed using a certified reference material because there is no certified reference material for vinegar. However, a certified reference material of bovine liver furnished by the National Institute of Standard and Technology was analysed, which has certified value for cadmium of $(0.50 \pm 0.03 \text{ μg g}^{-1})$. Using the proposed method was found cadmium content of $(0.48 \pm 0.03 \text{ μg g}^{-1})$.

Cadmium was also simultaneously determined in a vinegar sample using the analyte addition technique by the direct method proposed and by external calibration technique. The results obtained (expressed as confidence interval at 95% level) were as follow: $68.64 \pm 6.97$ and $65.49 \pm 5.10$ ng L$^{-1}$, respectively.

### 3.3. Application – determination of cadmium in vinegar

The direct method proposed herein was used for the quantification of cadmium in six vinegar samples purchased in supermarkets in Salvador City, Brazil. All the results obtained (expressed as 95% confidence intervals) are shown in Table 5. The cadmium contents of these six samples varied from 20 to 880 ng L$^{-1}$.

These six samples were also analysed by acid digestion method, using a reflux system and then analysed by ET AAS. The results presented in Table 5 were compared using statistical methods, and it was concluded that there is no difference between the results

**Table 4**
Box Behnken design – optimization of the experimental conditions for cadmium determination.

| Exp. | Py-t | Py-time | At-t | Modifier mass | Abs | QEI | Abs-n | QEI-n | Response multiple |
|---|---|---|---|---|---|---|---|---|---|
| 1 | −1 (500) | −1 (6) | 0 (1800) | 0 (3) | 0.04197 | 0.04819 | 0.9491 | 0.6711 | 1.6202 |
| 2 | 1 (900) | −1 (6) | 0 (1800) | 0 (3) | 0.03170 | 0.05055 | 0.7169 | 0.7039 | 1.4814 |
| 3 | −1 (500) | 1 (10) | 0 (1800) | 0 (3) | 0.04183 | 0.04863 | 0.9460 | 0.6772 | 1.6814 |
| 4 | 1 (900) | 1 (10) | 0 (1800) | 0 (3) | 0.02345 | 0.04803 | 0.5303 | 0.6688 | 1.2567 |
| 5 | 0 (700) | 0 (8) | −1 (1600) | −1 (2) | 0.04241 | 0.02660 | 0.9591 | 0.3704 | 1.3614 |
| 6 | 0 (700) | 0 (8) | 1 (2000) | −1 (2) | 0.04073 | 0.06479 | 0.9211 | 0.9022 | 1.9010 |
| 7 | 0 (700) | 0 (8) | −1 (1600) | 1 (4) | 0.04342 | 0.01987 | 0.9819 | 0.2767 | 1.2824 |
| 8 | 0 (700) | 0 (8) | 1 (2000) | 1 (4) | 0.03797 | 0.07181 | 0.8587 | 1 | 1.9447 |
| 9 | 0 (700) | 0 (8) | 0 (1800) | 0 (3) | 0.04175 | 0.05866 | 0.9441 | 0.8169 | 1.8313 |
| 10 | −1 (500) | 0 (8) | 0 (1800) | −1 (2) | 0.03874 | 0.04839 | 0.8761 | 0.6739 | 1.6079 |
| 11 | 1 (900) | 0 (8) | 0 (1800) | −1 (2) | 0.01991 | 0.03741 | 0.4503 | 0.5210 | 1.0160 |
| 12 | −1 (500) | 0 (8) | 0 (1800) | 1 (4) | 0.04422 | 0.03769 | 1 | 0.5249 | 1.5701 |
| 13 | 1 (900) | 0 (8) | 0 (1800) | 1 (4) | 0.02620 | 0.04402 | 0.5925 | 0.6130 | 1.2583 |
| 14 | 0 (700) | −1 (6) | −1 (1600) | 0 (3) | 0.04342 | 0.01773 | 0.9819 | 0.2469 | 1.2501 |
| 15 | 0 (700) | 1 (10) | −1 (1600) | 0 (3) | 0.04262 | 0.02359 | 0.9638 | 0.3285 | 1.3206 |
| 16 | 0 (700) | −1 (6) | 1 (2000) | 0 (3) | 0.03816 | 0.06612 | 0.8630 | 0.9208 | 1.8630 |
| 17 | 0 (700) | 1 (10) | 1 (2000) | 0 (3) | 0.03824 | 0.06522 | 0.8648 | 0.908 | 1.8511 |
| 18 | 0 (700) | 0 (8) | 0 (1800) | 0 (3) | 0.04283 | 0.05265 | 0.9686 | 0.7332 | 1.7648 |
| 19 | −1 (500) | 0 (8) | −1 (1600) | 0 (3) | 0.03980 | 0.02049 | 0.9001 | 0.2853 | 1.2099 |
| 20 | 1 (900) | 0 (8) | −1 (1600) | 0 (3) | 0.02276 | 0.02256 | 0.5147 | 0.3142 | 0.8560 |
| 21 | −1 (500) | 0 (8) | 1 (2000) | 0 (3) | 0.03653 | 0.06869 | 0.8261 | 0.9566 | 1.8650 |
| 22 | 1 (900) | 0 (8) | 1 (2000) | 0 (3) | 0.02255 | 0.05830 | 0.5099 | 0.8119 | 1.3917 |
| 23 | 0 (700) | −1 (6) | 0 (1800) | −1 (2) | 0.04328 | 0.05553 | 0.9787 | 0.7733 | 1.8185 |
| 24 | 0 (700) | 1 (10) | 0 (1800) | −1 (2) | 0.04148 | 0.06008 | 0.9380 | 0.8367 | 1.8466 |
| 25 | 0 (700) | −1 (6) | 0 (1800) | 1 (4) | 0.04380 | 0.04594 | 0.9905 | 0.6397 | 1.6852 |
| 26 | 0 (700) | 1 (10) | 0 (1800) | 1 (4) | 0.04086 | 0.04931 | 0.9240 | 0.6867 | 1.6698 |
| 27 | 0 (700) | 0 (8) | 0 (1800) | 0 (3) | 0.04376 | 0.05403 | 0.9896 | 0.7524 | 1.8068 |

Py-t: pyrolysis temperature; At-t: atomization temperature; Py-time: pyrolysis time; Abs: integrated absorbance; QEI: qualitative evaluation index; Abs-n; normalisation of the integrated absorbance; QEI-n: normalisation of the qualitative evaluation index.

**Table 5**
Determination of cadmium in vinegar by ETAAS.

| Sample | Cadmium content by direct method ($ng\,L^{-1}$) | Standard deviation | RSD (%) | Observation number | Cadmium determined after complete acid digestion[a] ($ng\,L^{-1}$) | Standard deviation |
|---|---|---|---|---|---|---|
| AV1 | 47.50 ± 1.60 | 0.64 | 1.35 | 3 | 48.49 ± 1.27 | 0.51 |
| AV2 | 880 ± 19 | 20.54 | 2.33 | 7 | 890 ± 10 | 4.02 |
| AV3 | 27.86 ± 1.09 | 0.44 | 1.58 | 3 | 28.78 ± 0.25 | 0.10 |
| AV4 | 47.55 ± 0.47 | 0.51 | 1.07 | 7 | 45.92 ± 0.90 | 0.36 |
| AV5 | 24.98 ± 1.02 | 0.41 | 1.64 | 3 | 24.57 ± 0.82 | 0.33 |
| AV6 | 20.31 ± 0.97 | 0.39 | 1.92 | 3 | 20.01 ± 1.02 | 0.41 |

[a] $N = 3$.

found by the direct method and those found by acid digestion with a reflux system.

The cadmium content found is in agreement with the data reported in the literature (Acosta, Diaz, Hardisson, & Gonzalez, 1993; Saei-Dehkordi et al., 2012).

## 4. Conclusions

In this study, a new multiple chemometric response function was established to qualitatively and quantitatively evaluate the analytical signals obtained during the multivariate optimization of the method proposed for the direct determination of cadmium concentrations in vinegar by ET AAS.

The multiple chemometric response function generated models that were validated and had good fits.

The direct method proposed is precise and accurate and has a limit of quantification that is sufficiently low for the determination of cadmium concentrations in vinegar.

The use of cold finger allows a complete digestion of vinegar samples using nitric acid and hydrogen peroxide for the determination of cadmium.

The cadmium contents of the six analysed samples were lower than the maximum limit allowed for foods by Brazilian regulations.

The determination of cadmium in certified reference material of bovine liver demonstrated that this method can be employed for quantification of cadmium in others matrices.

## Acknowledgements

## References

Acosta, A., Diaz, C., Hardisson, A., & Gonzalez, D. (1993). Levels of Cd, Pb, and Ni in different types of vinegars. *Bulletin of Environmental Contamination and Toxicology B, 51*, 852–856.

Da Silva, D. G., Junior, M. M. S., Silva, L. O. B., Portugal, L. A., Matos, G. D., & Ferreira, S. L. C. (2011). Determination of cadmium in rice by electrothermal atomic absorption spectrometry using aluminum as permanent modifier. *Analytical Methods, 3*, 2495–2500.

De Oliveira, S. R., & Gomes Neto, J. A. (2007). Evaluation of Bi as internal standard to minimize matrix effects on the direct determination of Pb in vinegar by graphite furnace atomic absorption spectrometry using Ru permanent modifier with co-injection of Pd/Mg(NO3). *Spectrochimica Acta Part B, 62*, 1046–1050.

Derringer, G., & Suich, R. (1980). Simultaneous-optimization of several response variables. *Journal Quality Technology, 12*, 214–219.

Dessuy, M. B., Vale, M. G. R., Welz, B., Borges, A. R., Silva, M. M., & Martelli, P. B. (2011). Determination of cadmium and lead in beverages after leaching from pewter cups using graphite furnace atomic absorption spectrometry. *Talanta, 85*, 681–686.

Ferreira, S. L. C., Bruns, R. E., Ferreira, H. S., Matos, G. D., David, J. M., Brandão, G. C., et al. (2007). Box–Behnken design: An alternative for the optimization of analytical methods. *Analytica Chimica Acta, 597*, 179–186.

Ferreira, S. L. C., Portugal, L. A., Matos, G. D., da Silva, D. G., de Jesus, R. M., & Brito, G. B. (2011). Aluminium as chemical modifier for the determination of lead in sugar cane spirits using electrothermal atomic absorption spectrometry. *Analytical Methods, 3*, 1168–1171.

Ferreira, S. L. C., Silva, L. O. B., de Santana, F. A., Junior, M. M. S., Matos, G. D., & dos Santos, W. N. L. (2013). A review of reflux systems using cold finger for sample preparation in the determination of volatile elements. *Microchemical Journal, 106*, 307–310.

Garcia-Rodrigues, D., Cela-Torrijos, R., Lorenzo-Ferreira, R. A., & Carro-Diaz, A. M. (2012). Analysis of pesticide residues in seaweeds using matrix solid-phase dispersion and gas chromatography–mass spectrometry detection. *Food Chemistry, 135*, 259–267.

Khajeh, M. (2011). Response surface modelling of lead pre-concentration from food samples by miniaturised homogenous liquid–liquid solvent extraction: Box–Behnken design. *Food Chemistry, 129*, 1832–1838.

Kishore, D., & Kayastha, A. (2012). Optimisation of immobilisation conditions for chick pea beta-galactosidase (CpGAL) to alkylamine glass using response surface methodology and its applications in lactose hydrolysis. *Food Chemistry, 134*, 1650–1657.

Lima, D. C., Matos, G. D., Barbosa, J. T. P., Grassi, M. T., Korn, M. G. A., de Andrade, J. B., et al. (2013). A separation system for lead fractionation in river water using electrothermal atomic absorption spectrometry. *Journal of Analytical Atomic Spectrometry, 28*, 156–160.

Ndung'u, K., Hibdon, S., & Flegal, A. R. (2004). Determination of lead in vinegar by ICP-MS and GFAAS: Evaluation of different sample preparation procedures. *Talanta, 64*, 258–263.

Ndung'u, K., Hibdon, S., & Flegal, A. R. (2007). Lead in vinegar: Determination and possible sources. *American Laboratory, 39*, 30.

Oliveira, S. R., Oliveira, A. P., & Gomes Neto, J. A. (2007). Tungsten permanent chemical modifier with co-injection of Pd(NO3)(2) + Mg(NO3)(2) for direct determination of Pb in vinegar by graphite furnace atomic absorption spectrometry. *Food Chemistry, 105*, 236–241.

Saei-Dehkordi, S. S., Fallah, A. A., & Ghafari, E. (2012). Determination of lead, cadmium, copper, and zinc content in commercial Iranian vinegars using stripping chronopotentiometry. *Food Analytical Methods, 5*, 767–773.

Singh, N., Srivastava, G., Talat, M., Raghubanshi, H., Srivastava, O. N., & Kayastha, A. M. (2014). Cicer alpha-galactosidase immobilization onto functionalized graphene nanosheets using response surface method and its applications. *Food Chemistry, 142*, 430–438.

Tarley, C. R. T., Lima, G. F., Nascimento, D. R., Assis, A. R. S., Ribeiro, E. S., Diniz, K. M., et al. (2012). Novel on-line sequential preconcentration system of Cr(III) and Cr(VI) hyphenated with flame atomic absorption spectrometry exploiting sorbents based on chemically modified silica. *Talanta, 100*, 71–79.

Zarena, A. S., Sachindra, N. M., & Udaya Sankar, K. (2012). Optimisation of ethanol modified supercritical carbon dioxide on the extract yield and antioxidant activity from *Garcinia mangostana* L.. *Food Chemistry, 130*, 203–208.